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THE EFFECT OF  $\text{CO}_2$  PRESSURE ON THE RATE  
OF DECOMPOSITION OF CALCITE

Taghi Darroudi  
(M.S. thesis)

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EFFECT OF CO<sub>2</sub> PRESSURE ON THE RATE  
OF DECOMPOSITION OF CALCITE (CaCO<sub>3</sub>)

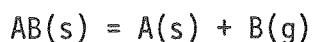
Taghi Darroudi  
Lawrence Berkeley Laboratory, University of California, Berkeley, CA  
ABSTRACT

The Langmuir method was employed to measure the rate of CO<sub>2</sub> escape from (10 $\bar{1}$ 1) cleavage surfaces of calcite (CaCO<sub>3</sub>) single crystals at temperatures from 893°K to 1073°K and at background pressures of CO<sub>2</sub> from  $10^{-5}P_{eq}$  to  $4 \times 10^{-2}P_{eq}$ , where  $P_{eq}$  is the equilibrium decomposition pressure. Rates of decomposition measured in vacuum were in good agreement with earlier studies carried out under similar conditions. The rates were relatively sensitive to the CO<sub>2</sub> pressure at pressures of the order of  $10^{-2}P_{eq}$ , but were essentially independent of CO<sub>2</sub> pressure for a range of lower pressures that cause a flux of CO<sub>2</sub> gas against the CaCO<sub>3</sub> sample surface up to about  $10^3$  times the flux that leaves the CaCO<sub>3</sub> in vacuum. In this latter CO<sub>2</sub> pressure range, the rate limiting process is probably a solid state diffusional step or surface step of CO<sub>2</sub>. The rate limiting process at CO<sub>2</sub> pressures near  $P_{eq}$  must be different, but more data are needed to determine what that process may be.

## INTRODUCTION

Because of the extensive use of CaO in industrial products and processes — such as cement, soda-lime-silica glasses, and refractories, as fluxes for steel refining and as getters for sulfur oxides in stack gases and coal — the decomposition of calcite by the reaction  $\text{CaCO}_3(\text{s}) = \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  has been studied by many investigators.<sup>1-7</sup>

It has usually been supposed that in endothermic decomposition reactions like  $\text{CaCO}_3$  decomposition, which have the general form



a surface or desorption step of the gaseous reaction product is the slowest step.<sup>7-10</sup> Recently, however, Searcy and Beruto<sup>11,12</sup> pointed out that a solid AB usually decomposes to yield a porous structure of the solid A and that in consequence the possibility must be considered that one of several other processes is rate limiting. The processes that they identified as necessary steps of the overall reaction included, in addition to a slow surface step of B (which might be its desorption), a) diffusion of the solid reaction component A in the plane normal to the reaction front, b) diffusion of the gaseous reaction component B in the plane normal to the advancing reaction front, and c) transfer of the solid reaction component across the interface between the solid phases AB and A. Figure 1 schematically illustrates this model.

The Searcy and Beruto analysis shows that if the spacing between adjacent CaO particles along the reaction front is small and if the rate limiting chemical step of the reaction is not highly irreversible, effusion of the gaseous product through the porous product layer may become

rate limiting after the initial phase of the reaction.<sup>12</sup> But in calcite decomposition, effusion of  $\text{CO}_2$  through the  $\text{CaO}$  product layer should not become rate limiting until the  $\text{CaO}$  layer thickness exceeds 1 mm.<sup>13</sup>

One reason that the calcite decomposition rate does not decrease as the  $\text{CaO}$  layer grows to thicknesses of the order of 1 mm is that the rate limiting chemical step is highly irreversible.<sup>5,13</sup> The theoretical analysis predicts<sup>12</sup> that if this irreversible chemical step involves  $\text{CO}_2$ , the decomposition rate should decrease linearly with increased  $\text{CO}_2$  pressure, but that if the irreversible step involves  $\text{CaO}$ , the rate should show a parabolic dependence on  $\text{CO}_2$  pressure.

Hyatt, Cutler, and Wadsworth<sup>4</sup> and Cremer and Nitsch<sup>7</sup> have reported that  $\text{CaCO}_3$  decomposition shows a parabolic dependence on  $\text{CO}_2$  pressure. These results would seem to identify movement of  $\text{CaO}$  as the rate limiting chemical step in  $\text{CaCO}_3$  decomposition. But the meaningful range for study of the effect of  $\text{CO}_2$  pressures extends from the equilibrium  $\text{CO}_2$  pressure for  $\text{CaCO}_3$  decomposition,  $P_{\text{eq}}$ , down to a  $\text{CO}_2$  pressure  $P_L$  that causes a flux of  $\text{CO}_2$  gas against the  $\text{CaCO}_3$  crystal equal to the flux that leaves the surface when the  $\text{CaCO}_3$  is decomposed in vacuum, that is the flux in a Langmuir experiment.<sup>14</sup> The  $\text{CO}_2$  pressure range between  $P_L$  and  $P_{\text{eq}}$  is about five orders of magnitude.  $\text{CO}_2$  pressures were varied only about a factor of ten at any fixed temperature in the study of Hyatt, et al. Cremer and Nitsch used a still more limited range of pressures and furthermore used powdered calcite samples for which the effects of particle size and bed depth are not well understood. The present study was designed to measure the effect of  $\text{CO}_2$  pressures from less than  $P_L = 10^{-5}P_{\text{eq}}$  to  $4 \times 10^{-2}P_{\text{eq}}$ .

about the highest relative pressure which it is practical to measure with the apparatus. The data are analyzed in terms of the model of Searcy and Beruto.

#### EXPERIMENTAL PROCEDURE

A natural calcite crystal was cleaved along its  $(10\bar{1}1)$  cleavage planes to yield slices 1 to 2 mm thick and about 7 mm in diameter. Spectroscopic analysis showed the principal metallic impurities of the crystal to be 0.08% Mn, 0.002% Mg, 0.005% Sr, 0.001% Cu, <0.005% Fe, <0.001% Ag, and <0.001% Ba.

Samples were suspended on a silica fiber from an arm of a Cahn R.G. Electrobalance, which had been calibrated with a 50 mg class M weight. The balance range used had a sensitivity of  $\sim 10 \mu\text{g}$ .

Figure 2 shows a cross-sectional drawing of the assembled apparatus. The heating elements were tungsten hairpin-shaped wires connected in parallel. To reduce temperature gradients and the contamination of the samples by condensable products of reaction of  $\text{CO}_2$  with the tungsten filaments, a platinum cylinder 3 cm in diameter and 10 cm long was placed around the sample. Temperatures were measured with a Pt/Pt-10%Rh thermocouple placed with its junction immediately below the sample. Temperatures read with this thermocouple were corrected for the difference between its temperature and that of a similar thermocouple that was placed for a calibration run in the position subsequently occupied by the calcite crystals.

The sample chamber could be evacuated to a residual pressure of  $<2 \mu\text{torr}$  during decomposition. When runs were to be made in  $\text{CO}_2$ , the diffusion pump was turned off and  $\text{CO}_2$  was held at a steady state level

by adjusting a leak valve. Pressures were measured with an ion gauge.

## RESULTS AND DISCUSSION

In a previous study, when a calcite crystal was masked so that only part of a single face was exposed, the decomposition rate remained constant until about 75% of the crystal had decomposed.<sup>5</sup> In the present study, decomposition occurred over the entire crystal surface. To insure that measurements were dependent only on CO<sub>2</sub> pressure and not upon the extent of reaction, decomposition rates were measured in vacuum for calcite slices of two different thicknesses (Fig. 3). These runs show that some 50% of the crystals could be decomposed in vacuum before the rates of decomposition decreased significantly.

Figure 4 compares kinetic data obtained as a function of temperature in vacuum in the present study to data of two previous studies in this laboratory.<sup>5,15</sup> The kinetic data are reported in terms of the pressure inside an ideal effusion orifice that would yield the flux of CO<sub>2</sub> that is found to leave the crystals. These equivalent pressures are calculated from the Hertz-Knudsen-Langmuir equation:<sup>14</sup>

$$P_L = J(2\pi MRT)^{1/2}$$

where J is the observed flux density, P<sub>L</sub> is the equivalent pressure, M is the molecular weight of the gas, R is the gas constant and T is the absolute temperature. The line described in the figure caption as a least squares fit to data measured in the present study was calculated from data obtained in a single heating in vacuum which yielded the points shown by open circles. The points marked by triangles were measured in vacuum at the beginning of isothermal runs at varied CO<sub>2</sub>

pressures. The differences in fluxes reported in the three investigations may result from calibration errors, but may also be a consequence of as yet unidentified effects of small differences in composition or crystal imperfections on the rates.

The ratio of the apparent decomposition pressures  $P_L$  to the equilibrium decomposition pressure  $P_{eq}$  is a useful measure of the irreversibility of the reaction, just as is the corresponding pressure ratio for congruent vaporization.<sup>5</sup> The ratio is 1 for a completely reversible reaction. For calcite decomposition these three studies agree in showing that  $P_L/P_{eq} \approx 10^{-5}$ . The apparent enthalpy of activation for the decomposition calculated from the temperature dependence of  $\ln P_L = -(\Delta H^*/RT) + (\Delta S^*/R)$ , using  $P_L$  values measured in the isothermal run of this study is  $52.6 \pm 5$  kcal. The best value that can at present be set for  $\Delta H^*$  is  $50 \pm 3$  kcal.<sup>15</sup>

It is only possible to compare qualitatively the pressure dependence found for the  $CO_2$  decomposition fluxes in the present study to measurements of Hyatt, et al.<sup>4</sup> and of Cremer and Nitsch,<sup>7</sup> because the Hyatt data are reported only as points on a small scale plot, and Cremer and Nitsch worked with powders. Figure 5 shows the fluxes of  $CO_2$  measured as functions of the pressure of  $CO_2$  at 983°K and at 1006°K in the present research. The sharp change in slope at low  $CO_2$  pressures might be interpreted as consistent with a parabolic dependence of flux on  $CO_2$  pressure, but at higher  $CO_2$  pressures the dependence of flux on pressure might more reasonably be described as linear. Furthermore, when the measurements are extended to pressures which are much lower than shown in Fig. 5, but which give  $CO_2$  fluxes against the calcite crystal which are still an order of magnitude

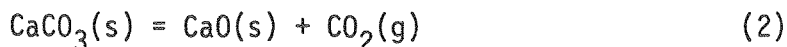


or more higher than the net decomposition flux, the  $\text{CO}_2$  flux is not much more increased, (Figs. 6-9).

The low pressure regime is clearly not characterized by a parabolic dependence of decomposition rate on the  $\text{CO}_2$  pressure,  $P_{\text{CO}_2}$ , but instead is better described by an equation of the form

$$J = k(P_{\text{eq}} - P_{\text{CO}_2}). \quad (1)$$

$P_{\text{CO}_2}$  is negligible in this low pressure range, so  $J \cong kP_{\text{eq}}$ . This kind of pressure dependence implies that the rate limiting process is either solid state diffusion of  $\text{CO}_2$  or a surface step for  $\text{CO}_2$ .<sup>12</sup> The possibility that the final desorption step of  $\text{CO}_2$  is rate limiting can be eliminated by comparison of the apparent activation entropy to the entropy of the reaction  $\text{CaCO}_3(\text{s}) = \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$



Even if  $\text{CaO}$  is produced in a thermodynamically active state, its entropy would not differ by more than 2 or 3 cal/mole-degree from the entropy of normal  $\text{CaO}$ . Therefore, if desorption of  $\text{CO}_2$  were rate limiting, the transition state would have properties close to those of the separate  $\text{CaO}$  phase plus  $\text{CO}_2$  gas, and the apparent entropy of activation should be close to the entropy of reaction 2. The apparent entropy of activation  $\Delta S^*$  can be calculated from the measured apparent activation enthalpy,  $50 \pm 3$  kcal,<sup>15</sup> and the values of  $P_L$  in Fig. 4 by means of the relation

$$\ln P_L = - \frac{\Delta H^*}{RT} + \frac{\Delta S^*}{R}$$

If the value of the Powell and Searcy plot at 1000°K is used,  $\Delta S^*$  is calculated to be 20.5 cal/mole-deg., which is much lower than the entropy of reaction 2, 35 cal/mole-deg. at 1000°K.

The change in the functional dependence of decomposition flux on  $\text{CO}_2$  pressure at higher  $\text{CO}_2$  pressures indicates that the rate limiting process is changed in that pressure range. Until measurements can be extended to pressures closer to  $P_{\text{eq}}$ , it is not possible to decide whether or not the dependence is parabolic in the high pressure range. Ewing et al.<sup>16</sup> have shown that the surface area of the CaO produced by reaction 2 is a strong function of the  $\text{CO}_2$  pressure in about the same pressure range that shows the strong influence of  $\text{CO}_2$  pressure on the decomposition rate. It may be that the decomposition kinetics at high  $\text{CO}_2$  pressures are influenced by changes in the geometry of the CaO-CaCO<sub>3</sub> interface.

Reason for believing that the CaO particle size and the rate of decomposition may be inter-related is given by the influence found of the sequence of pressures on the resultant decomposition flux (Figs. 6-9). Duplicate runs shown in Figs. 6 and 7 are reasonably reproducible. Data for these runs were taken by initiating decomposition in vacuum and making subsequent measurements at higher pressures. When pressures were then decreased (Fig. 7) fluxes fell below those measured before. A still more dramatic effect of pressure sequence is shown in Fig. 9. Here the initial flux, measured at relatively high  $\text{CO}_2$  pressures, falls well below the flux that was measured in the same general pressure range after the sample had been decomposed for a time in vacuum. It is evident that clarification of the decomposition kinetics at high relative  $\text{CO}_2$  pressures will require careful attention to the influence of sample history on the rate.

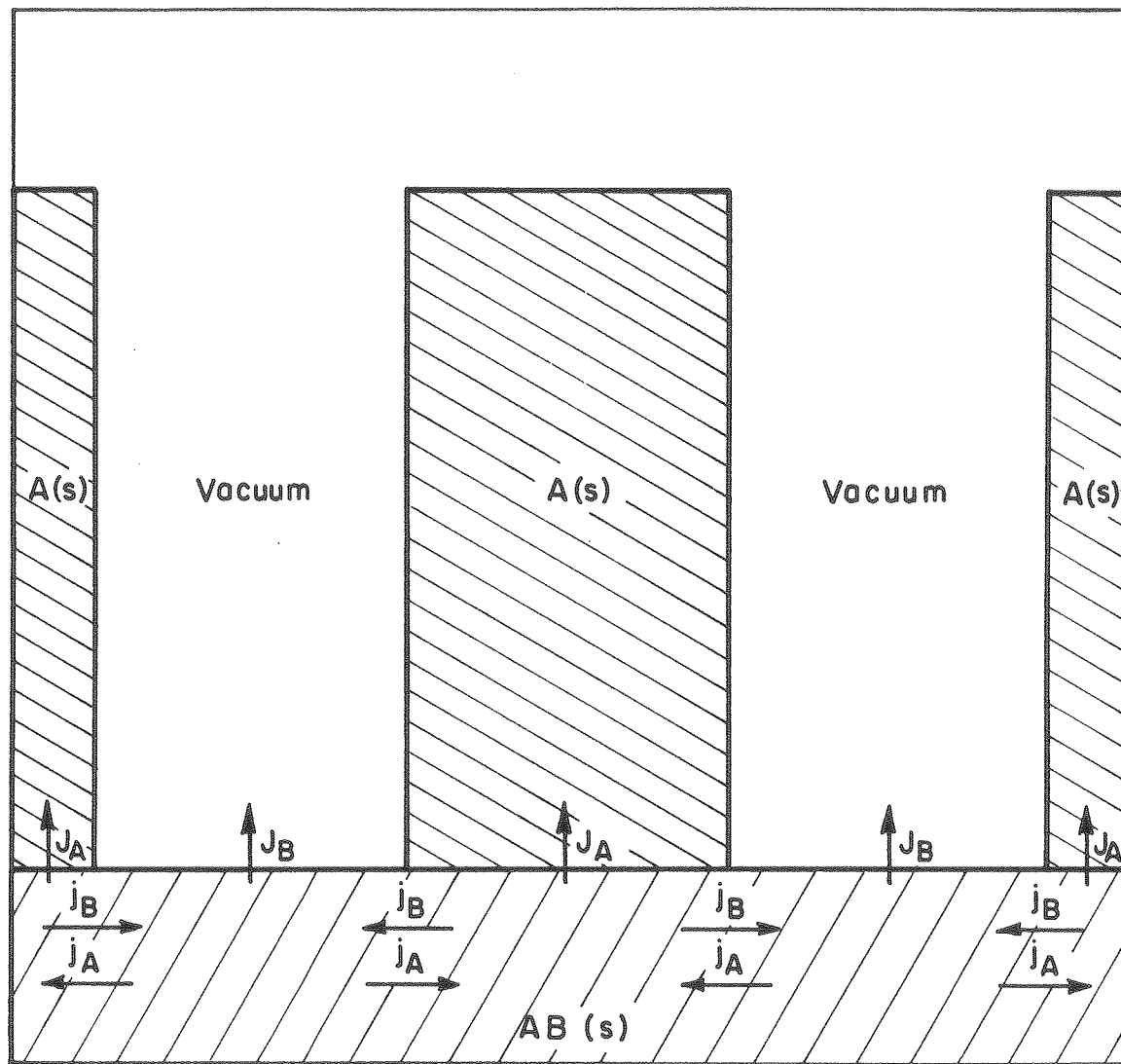
#### ACKNOWLEDGMENT

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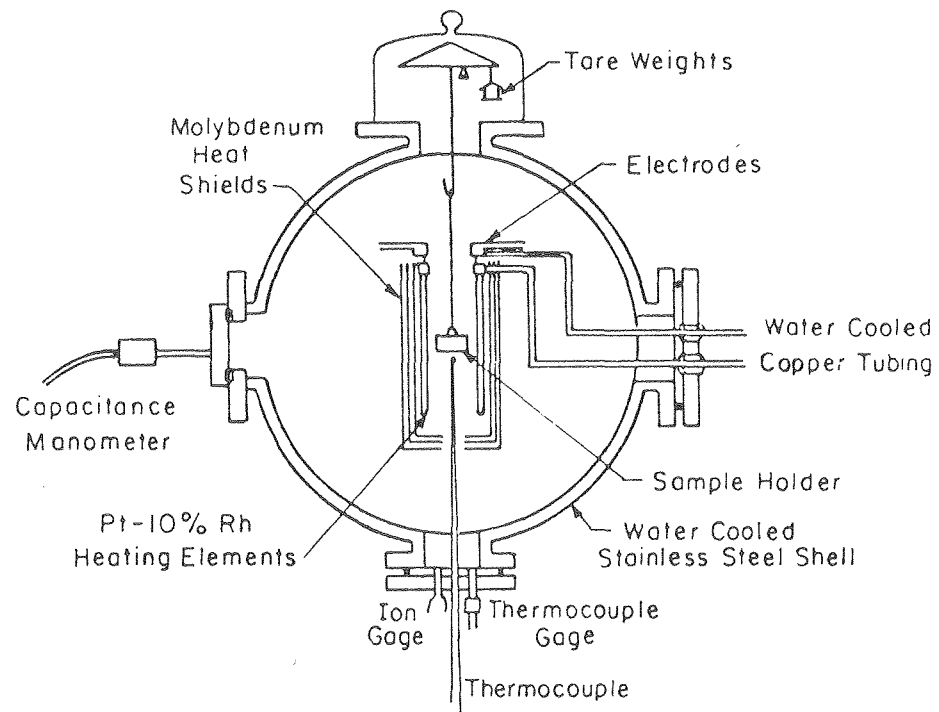
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FIGURE CAPTIONS

1. Schematic drawing of the cross-section of a partially decomposed particle of solid AB. The fluxes of A and B particles  $j_A$  and  $j_B$  must move in the plane perpendicular to the advancing interface in order for particles of solid A and pores to replace volume elements of AB phase. Fluxes  $J_A$  of A molecules must cross the interface between AB(s) and the product solid phase A and fluxes  $J_B$  are transferred from AB(s) to the vapor phase.
2. Cross-sectional drawing of the apparatus.
3. Decomposition rates measured as a function of time for two  $\text{CaCO}_3$  crystals that differed by about a factor of 2 in mass.
4. Values found for the  $\text{CO}_2$  flux from  $\text{CaCO}_3$  decomposed in vacuum. The open circles are data collected in a single run in vacuum; the triangles are initial points measured in isothermal runs in which  $\text{CO}_2$  background pressures were varied. The line --- is a least squares fit for this run. The solid line is from Beruto and Searcy<sup>5</sup> and the dashed line is from Powell and Searcy.<sup>15</sup>
5. Flux of  $\text{CO}_2$  plotted versus  $P_{\text{CO}_2}$  at 983°K and 1006°K.
6. Flux of  $\text{CO}_2$  versus  $\log P_{\text{CO}_2}$  measured in three runs at 983°K. Points numbered in order measured in each run.
7. Flux of  $\text{CO}_2$  versus  $\log P_{\text{CO}_2}$  at 1006°K. Points numbered in order measured.
8. Flux of  $\text{CO}_2$  versus  $\log P_{\text{CO}_2}$  at 1073°K. Points numbered in order measured.
9. Flux of  $\text{CO}_2$  versus  $\log P_{\text{CO}_2}$  at 898°K. Points numbered in order measured.

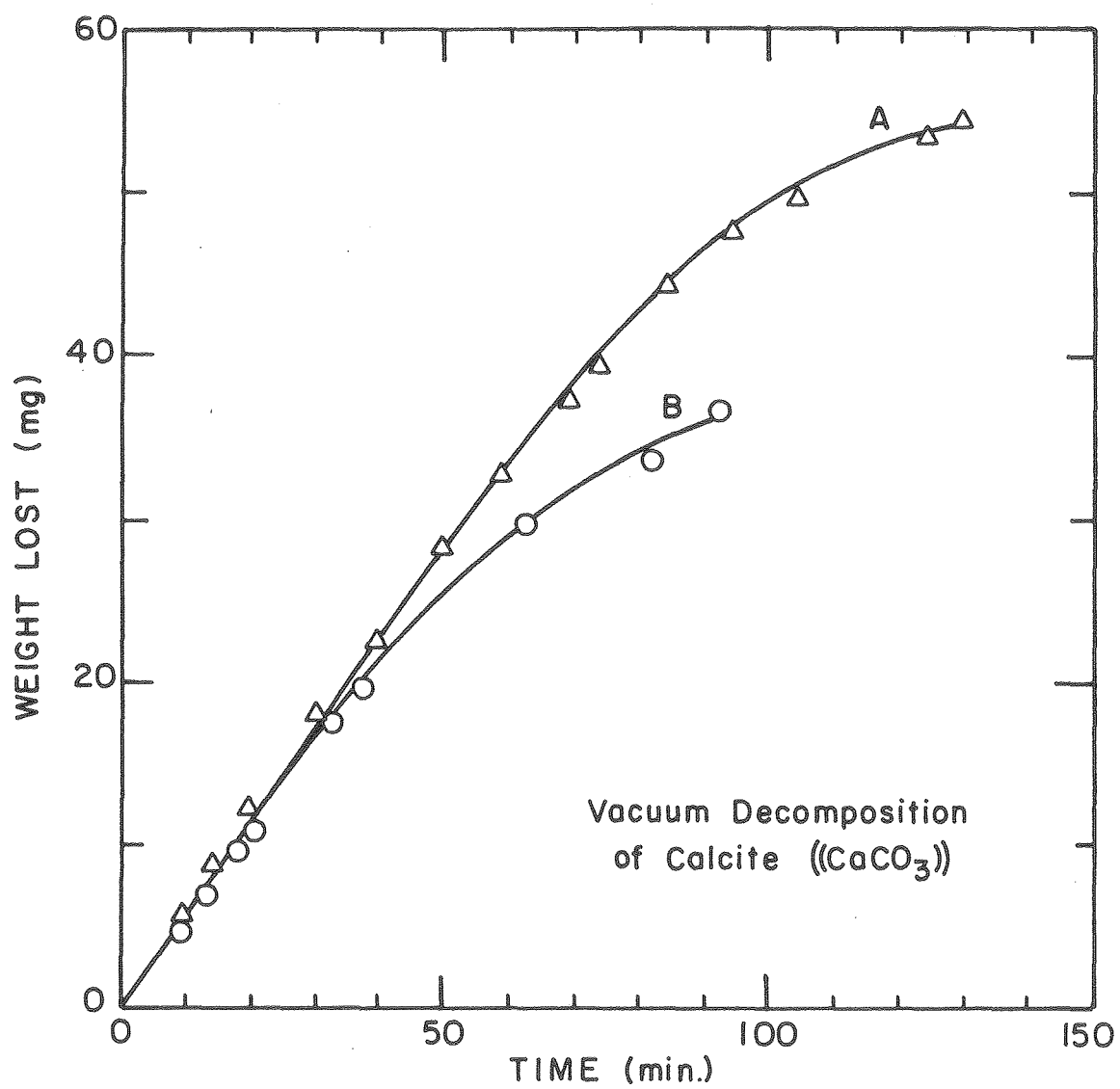


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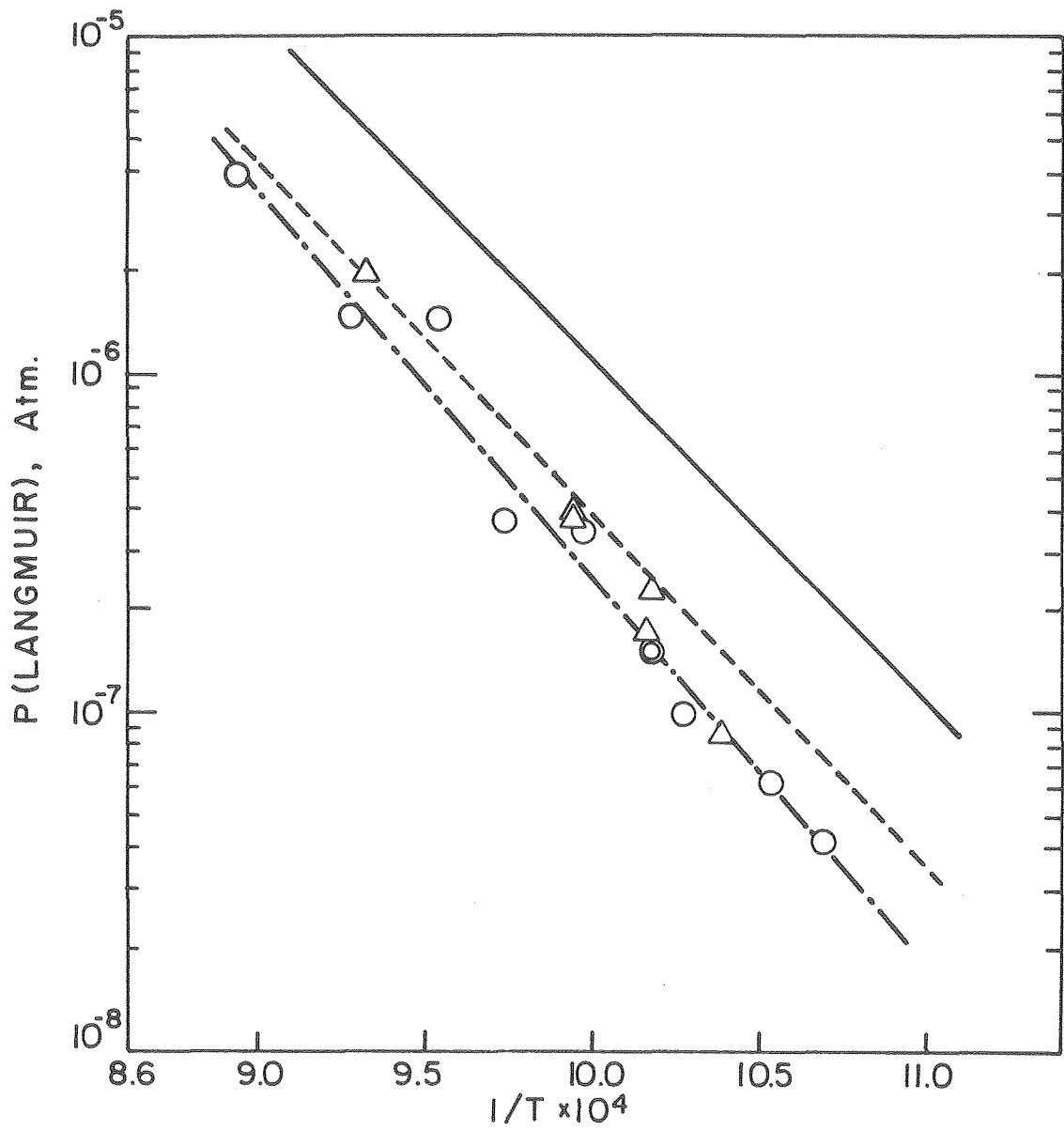


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Experimental apparatus for decomposing  $\text{CaCO}_3$

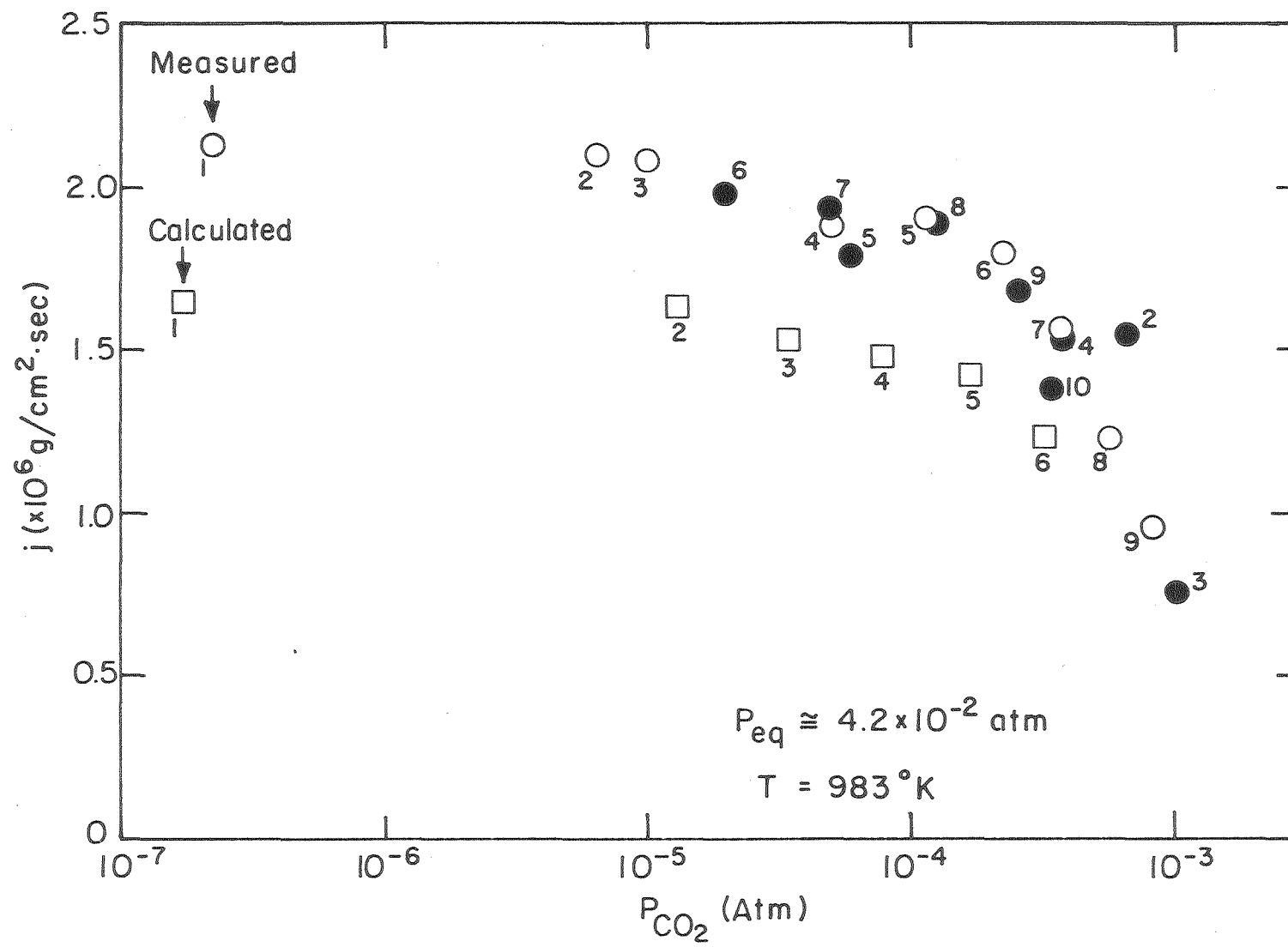


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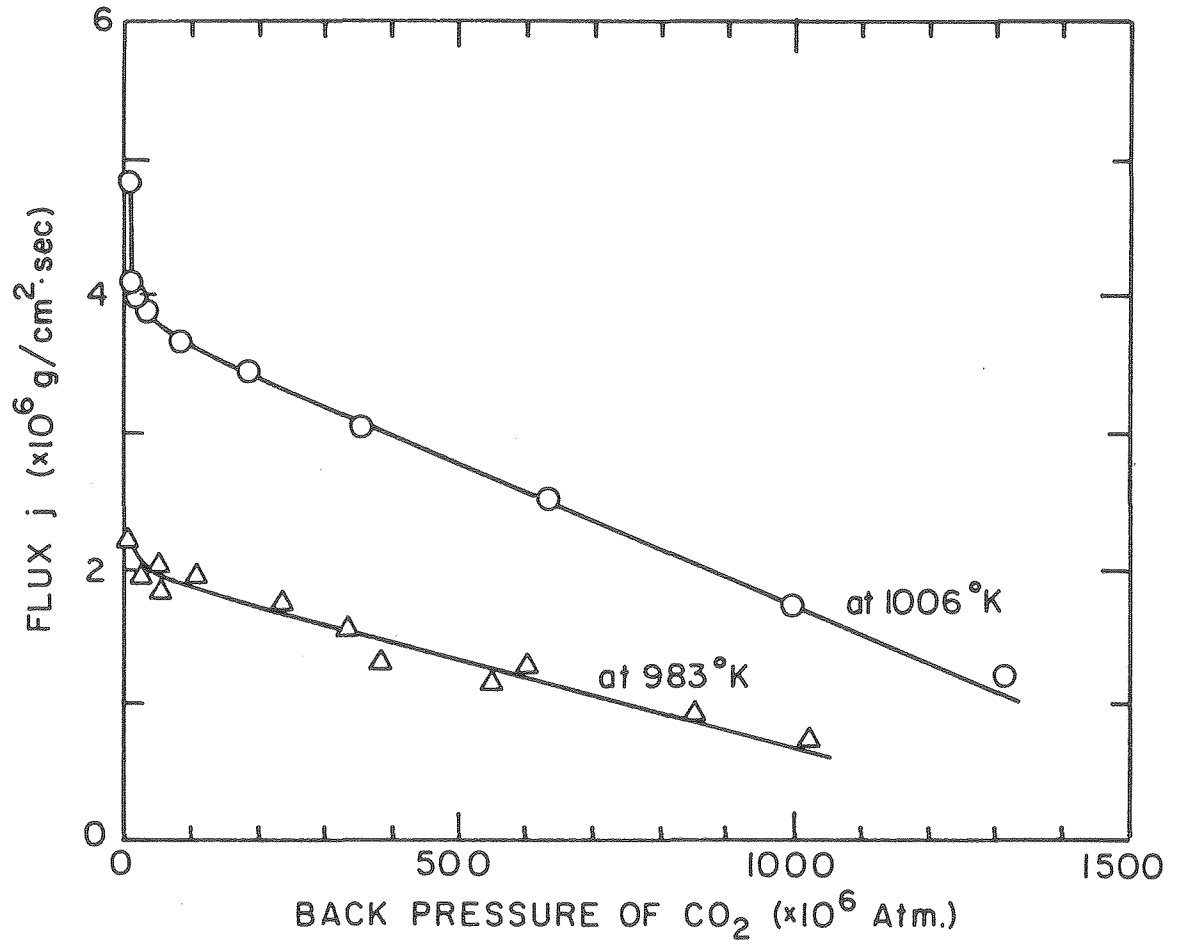


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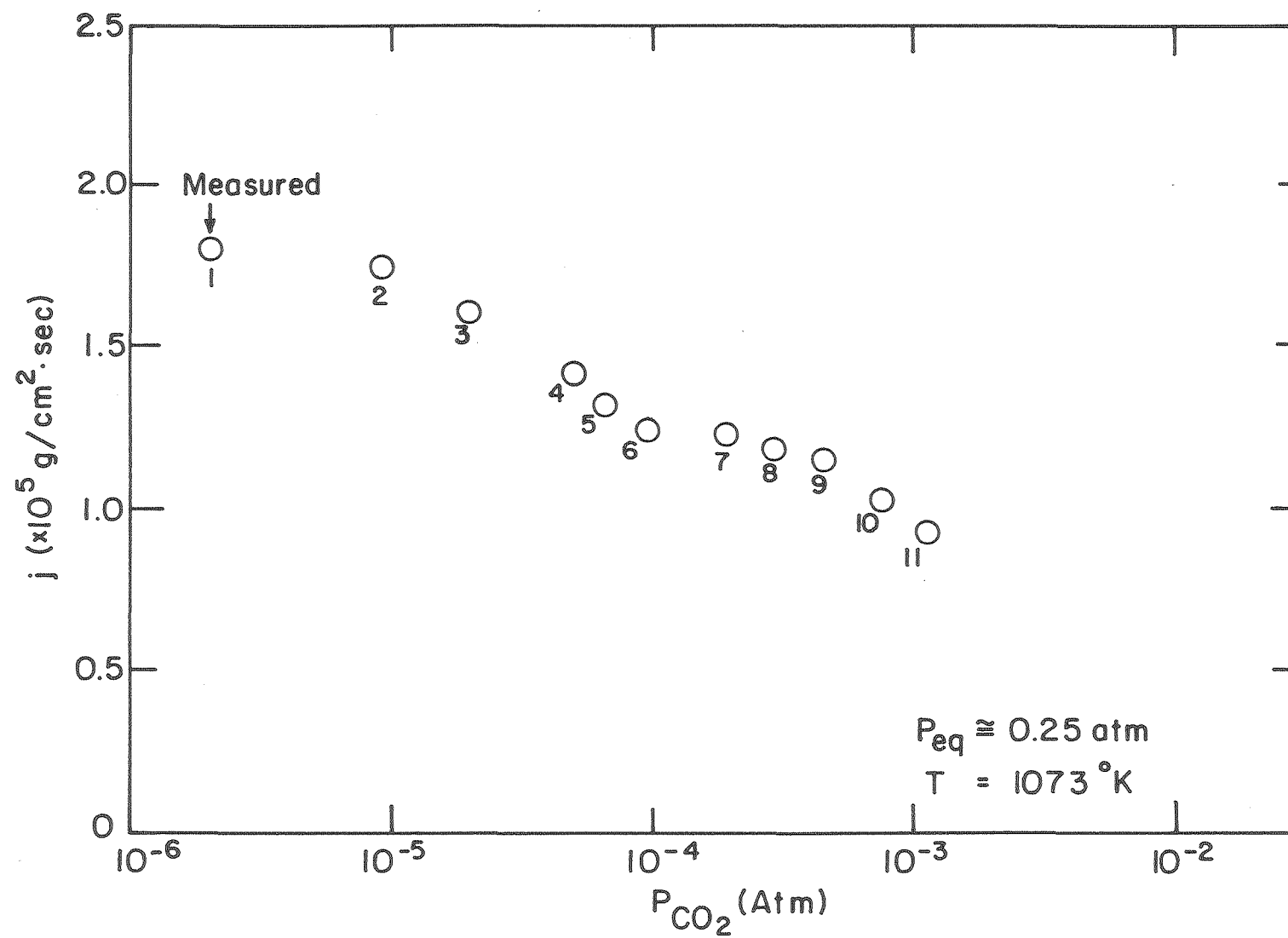




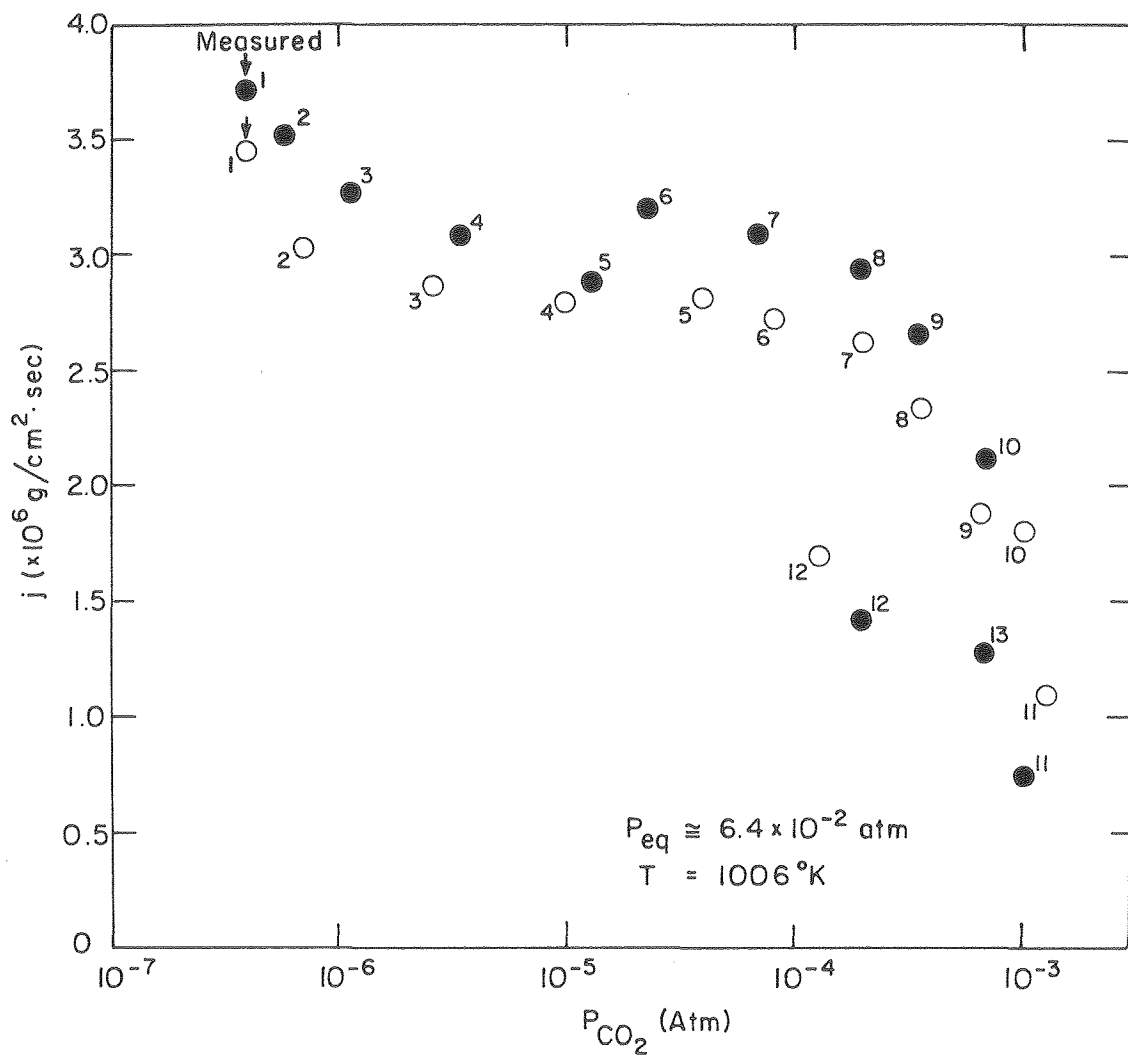
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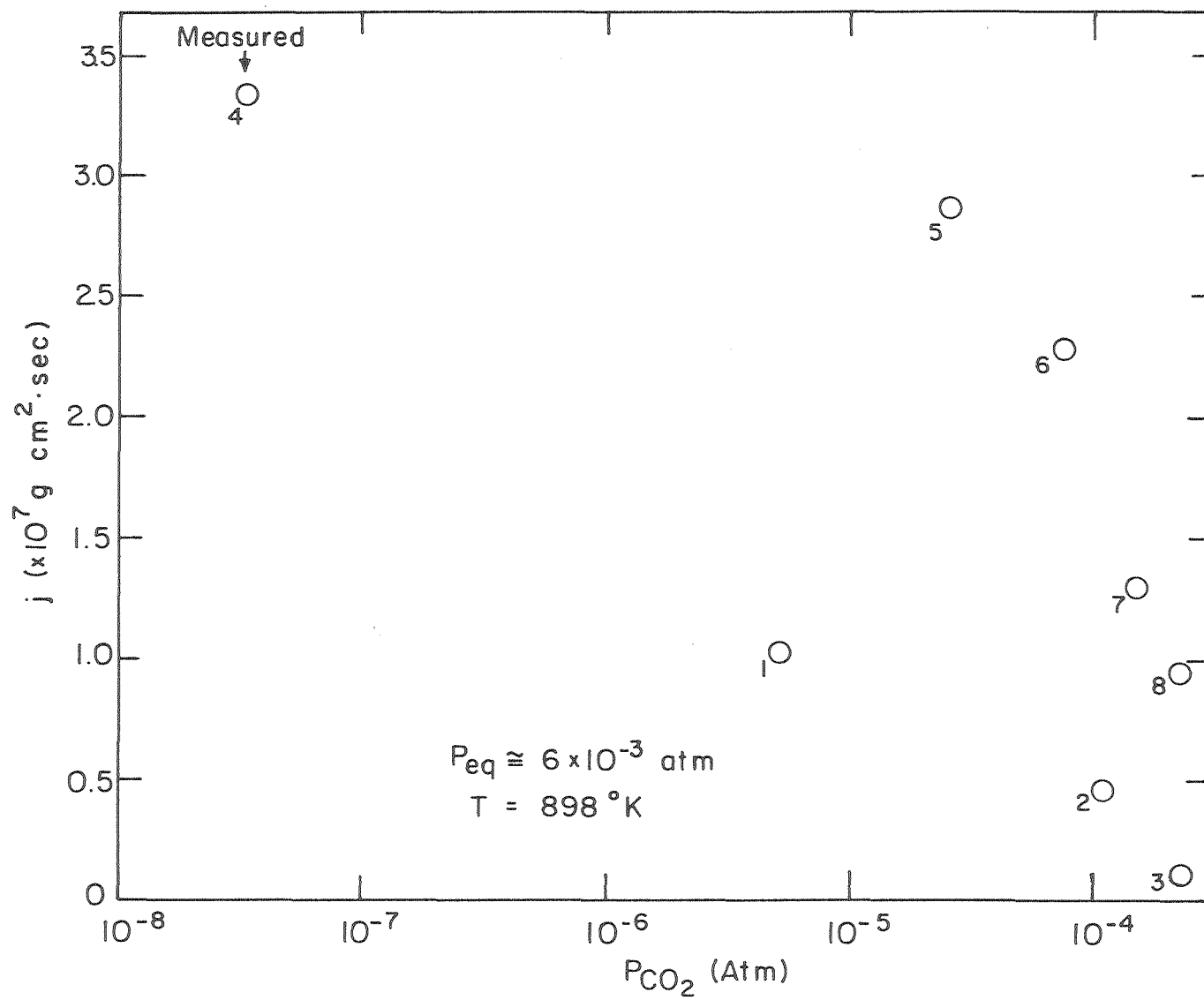
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